Local field effects on the radiative lifetimes of Ce^{3+} in different hosts

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Abstract

For emitters embedded in media of various refractive indices, different theoretical models predicted substantially different dependencies of the spontaneous emission lifetime on refractive index. It has been claimed that various measurements on $4f \to 4f$ radiative transition of Eu^{3+} in hosts with variable refractive index appear to favor the real-cavity model [J. Fluoresc. 13, 201 (2003) and references therein, Phys. Rev. Lett. 91, 203903 (2003)]. We notice that $5d \to 4f$ radiative transition of rare-earth ions, dominated by allowed electric-dipole transitions with line strengths less perturbed by the ligands, serves as a better test of different models. We analyze the lifetimes of $5d \to 4f$ transition of Ce^{3+} in hosts of refractive indices varying from 1.4 to 2.2. The results favor the macroscopic virtual-cavity model based on Lorentz local field [J. Fluoresc. 13, 201 (2003)].

I. INTRODUCTION

It is well known that radiative transition process of emitters in media differs from those in vacuum.[1,2] Because of fundamental importance and relevance to various applications in low-dimensional optical materials and photonic crystals, this issue continues to attract both theoretical and experimental attention.[3,4,5] Various macroscopic (see Ref.2 for a recent review) and microscopic[5,6,7] theoretical models have been developed to predict, among other optical properties, the spontaneous emission rates of lifetimes on refractive index. However, different models predict substantially different dependences of radiative lifetime on refractive index. The macroscopic model based on Lorentz local field, usually referred to as virtual-cavity model[2,5] has appeared in most textbooks and been used in calculations. Only limited experimental studies aimed specifically at discriminating between different models,[2,4] with results appear to support the real-cavity model.[8,9] It has also been pointed out that different models should apply under different circumstances.[2]

The underline assumption of all those models and experimental studies is that the only contribution to the spontaneous radiative lifetime is from the electric dipole moment whose strength does not vary (or changes in a predictable way) when surrounding media vary. We notice that the experimental results that have been claimed to support the real-cavity model[4,10,11] are all lifetimes of the $^5D_0$ level of Eu^{3+} in different hosts with varying refractive index. It is well-known that part of the radiative relaxation of $^5D_0$ (to $^7F_1$) is due to magnetic dipole moment, which has a different dependence on refractive index, and the electric dipole strength of $^5D_0$ to $^7F_2$ transition is hypersensitive to environment and may not be treated as a constant. In general, $4f \rightarrow 4f$ electric dipole radiative relaxation in rare-earth ions is due to mixing in $4f^N$ states with states with opposite parity, which depend strongly on the environment. Since this dependence is usually very difficult to be taken into account, lifetimes of $4f \rightarrow 4f$ radiative relaxation do not serve as a good examination of different models. In contrast, $5d \rightarrow 4f$ radiative transitions of rare-earth ions are dominated by allowed electric-dipole moment contributions, whose strengths are less perturbed by the environment and the line strengths for the radiative relaxation can be reliably predicted. Hence the lifetimes of $5d \rightarrow 4f$ radiative transitions give a better test of different models.

In this paper we analyze the lifetimes of $5d \rightarrow 4f$ transition of Ce^{3+} ions in hosts of different refractive indices and make a comparison between different models. In Sec. II we

derive the basic formula to calculate the line strength and lifetime of the d levels of Ce^{3+}. The lifetimes and energies of d levels of Ce^{3+} ions and the refractive indices are summarized and analyzed with different models in Sec. III.

II. $d \to f$ TRANSITION RATES OF CE^{3+} IN HOSTS

The general spontaneous radiative emission rate of electric dipole transition from an localized initial state I to a localized final state F can be written as[2]

$$\Gamma_{IF} = \frac{64\pi^4}{3h}\chi\nu_{IF}^3|\vec{\mu}_{IF}|^2, \tag{1}$$

where I and F and transition initial and final states, respectively, ν_{IF} is the emission wavenumber, $\vec{\mu_{IF}}$ is the electric dipole moment $-e\vec{r}$ between state I and F, and χ is an enhancement factor due to dielectric medium, which equals $n[(n^2+2)/3]^2$ for virtual- and $n[3n^2/(2n^2+1)]^2$ for real-cavity model. The lifetime of energy I can be calculated as the inverse of the total emission rate of I.

For the $5d \to 4f$ emission of Ce^{3+} ions, The eigenvectors of transition initial states are dominated by bases with only one electron in open shell $5d$ and the transition final states are dominated by bases with only one electron in open shell $4f$. it is tempting to approximate the electric dipole moment between a $5d$ state and a $4f$ state with the straightforward matrix element of electric dipole $-e\vec{r}$ between one particle orbitals $4f$ and $5d$. Such an approximation overestimate the radiative lifetime of Ce^{3+} free ion by a factor of about 3. Since the transition initial and final states are actually many-particle states, calculation[12] showed that configuration mixing needed to be taken into account to obtain correct radiative lifetime for Ce^{3+} free ion. For rare-earth ions in hosts, ligand polarization could also contribute to the radiative transition rate. Theoretical treatment of $f-d$ electric dipole moment of rare-earth ions taking all those corrections into account is not trivial, which can be found in Ref.13. For Ce^{3+} ions in hosts, since there is only one electron in the open shell, neglecting the small ligand polarization contribution, the correction due to configuration mixing is equivalent to reduce the radial integral $\langle 5d|\, r\, |4f\rangle$. For Ce^{3+} free ion, the effective radial integer is $\langle 5d|\, r\, |4f\rangle_{\text{eff}} = 0.025$nm.

For Ce^{3+} ions, since the splitting between different transition final states is much smaller than the average energy difference between the lowest $5d$ and $4f$ states, we can make an

approximation to the summation of Eq. (1) over final state F by replace the wave numbers with the average value $\bar{\nu}$. Under this approximation, the total spontaneous emission rate turns out to be independent of the wavefunction of the initial $5d$ state, and can be written as

$$\frac{1}{\tau_r} = \frac{64\pi^4 e^2 \chi |\langle 5d| r |4f\rangle_{\text{eff}}|^2 \bar{\nu}^3}{5h} \tag{2}$$

$$= 4.34 \times 10^{-4} |\langle 5d| r |4f\rangle_{\text{eff}}|^2 \chi \bar{\nu}^3 (s^{-1}), \tag{3}$$

where units for radial integral, $\bar{\nu}$ and τ_r are nm, cm^{-1} and sec, respectively. With measured τ_r and $\bar{\nu}$ values, we can derive measured values for $\langle 5d| r |4f\rangle^2 \chi$ ($\sim \tau_r^{-1}$) and compare them with the predictions of different model.

III. ANALYSIS OF RADIATIVE RELAXATION LIFETIMES OF CE^{3+} IN DIFFERENT HOSTS

The $5d \rightarrow 4f$ transitions of Ce^{3+} in various hosts have been widely studied due to applications as scintillators, tunable UV lasers and phosphors. The lifetimes, peak wavelengths of emission spectra and refractive indices of Ce^{3+} in different hosts are summarized in Table I. Some of the data are measured at room temperature and some are measured at low temperature. Ideally, we need work with the lifetimes for different hosts at the same low temperature, preferably at 0K. Fortunately, due to large separation between $5d$ and $4f$ states and strong electric dipole $5d - 4f$ radiative relaxation, nonradiative relaxations are negligible and the lifetimes at room temperature only change (decrease) slightly from low-temperature ones. In some experiments, the observed lifetimes at room temperature is even slightly longer than the low-temperature lifetimes due to reabsorption. We neglect all these small corrections and put a uncertainty of about 10% to the spontenous emission lifetime in the figure to guide eyes.

Since the transition rates depend not only on refractive index factors but also the emission energy, we cannot follow Ref.s 2,4 to compare experimental and theoretical lifetime-refractive index curves. Instead, the measured $\langle 5d| r |4f\rangle^2 \chi$ values are plot as a function of measured refractive index in Fig.1, together with calculated curves using two different models with $\langle 5d| r |4f\rangle_{\text{eff}}^2$ values obtained with experimental-value-weighted least-square fitting. It can be seen that the virtual-cavity model fits the measured data much better than

the real-cavity model, while the real-cavity model gives an almost linear dependence of the emission rates on refractive index, which cannot fit the measured data at all. This is in contrary to the conclusion draw from the $f - f$ transitions of Eu^{3+} in various hosts. The best-fit value for the effective radial integral is $\langle 5d|\, r \,|4f\rangle_{\text{eff}} = 0.0281$. This value is actually bigger than the free ion value 0.025, in contrary to expectations that it should be smaller than the free ion value.[14,15] Using the virtual-cavity model, the $\langle 5d|\, r \,|4f\rangle_{\text{eff}}$ for each hosts have been calculated and are given in Table I. It can be seen that most of the values are quite consistent.

IV. CONCLUSION

In conclusion, we analyze the spontaneous emission rates $5d \rightarrow 4f$ transition of Ce^{3+} in hosts of refractive indices between 1.4 to 2.2 with the two major models. The dependence of the rates on refractive indices favor the macroscopic virtual-cavity model based on Lorentz local field.[2] We also conclude that the values of Ce^{3+} effective radial integral $\langle 5d|\, r \,|4f\rangle_{\text{eff}}$ are larger in crystals than in vacuum.

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TABLE I: Summary of the radiative decay parameters for Ce^{3+} in various hosts, where $\tau_{\rm r}$ (unit: ns) is the measured lifetime of the lowest $5d$ state, which is dominated by radiative relaxation and used an spontaneous emission lifetime in this paper, λ (unit: nm) is the peak emission wavelength, n is refractive index, $\chi_{\rm virtual}$ and $\chi_{\rm real}$ are χ-factors for virtual- and real-cavity models, respectively, and $\langle 4f|\, r\, |5d\rangle_{\rm eff}$ (unit: nm) is derived from measured lifetime using Eq. (2) for virtual-cavity model.

[htp]

Host	Ref.	$\tau_{\rm r}$	λ	n	$\chi_{\rm virtual}$	$\chi_{\rm real}$	$\langle 4f|\, r\, |5d\rangle$
LaF_3	15	19	292	1.6	3.69	2.52	0.0286
LaF_3	16	21	300	1.6	3.69	2.52	0.0283
YAG	15	59.1	550	1.9	6.64	3.30	0.0312
YAG	17	65	550	1.9	6.64	3.30	0.0298
CaF_2	18	40	330	1.43	2.59	2.07	0.0282
$YAlO_3$	15	17.1	362	1.98	7.71	3.50	0.0288
$YLiF_4$	15	35.7	320	1.49	2.94	2.23	0.0268
Gd_2SiO_5	19	56	430	1.89	6.52	3.27	0.0224
Lu_2SiO_5	19	40	420	1.81	5.59	3.06	0.0276
Lu_2SiO_5	20	32	400	1.81	5.59	3.06	0.0287
Lu_2SiO_5	20	54	480	1.81	5.59	3.06	0.0290
$LuAlO_3$	19	18	365	1.94	7.16	3.40	0.0295
$Lu_2Si_2O_7$	19	38	385	1.74	4.88	2.88	0.0266
Li-Al-B glass	21	38	360	1.528	3.19	2.33	0.0298
$Sr_2B_5O_9Br$	22	38	390	1.65	4.08	2.64	0.0297
$Sr_2B_5O_9Br$	22	29	355	1.65	4.08	2.65	0.0295
$LiSrAlF_6$	23	28	292	1.41	2.49	2.02	0.0287
$LiCaAlF_6$	23	25	290	1.45	2.71	2.13	0.0288
CaS	24	36	562	2.12	9.93	3.86	0.0338
$SrGa_2S_4$	24	20	455	2.17	10.8	3.99	0.0316
BaF_2	25	30	320	1.475	2.85	2.19	0.0297
$Ca_2Al_2SiO_7$	26	40	410	1.68	4.34	2.73	0.0302
YPO_4	27	23	345	1.75	4.98	2.91	0.0287
Free ion	12	30	201	1	1	1	0.0250

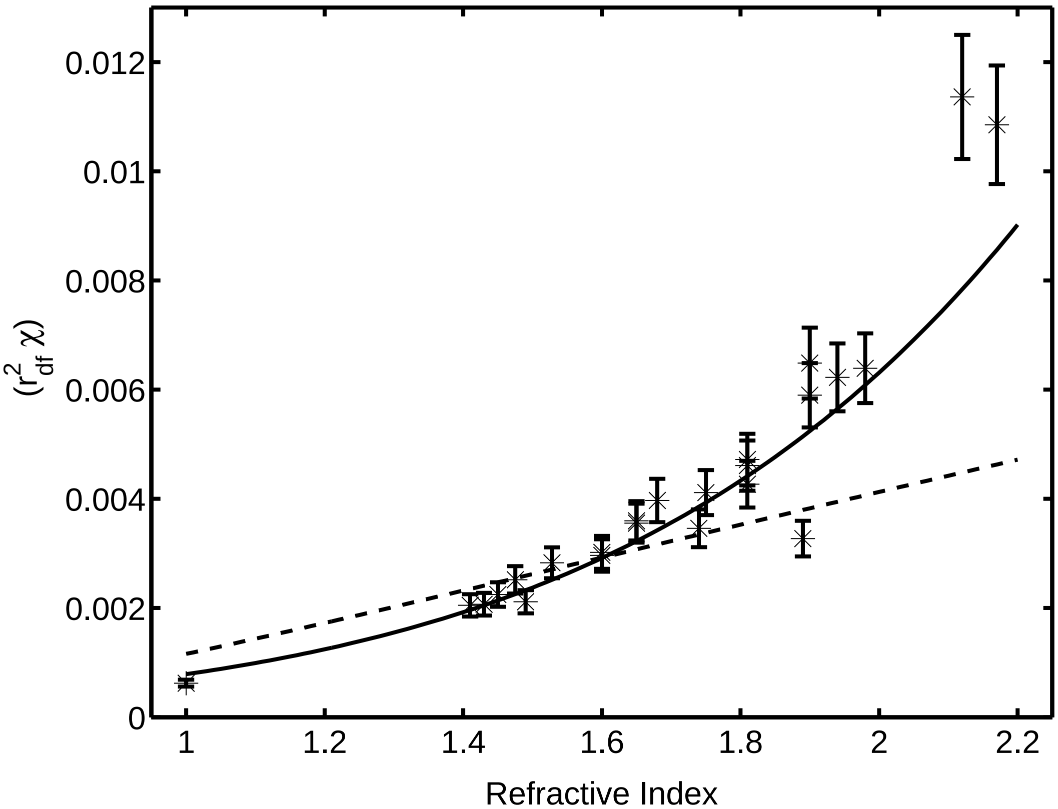

FIG. 1: Variation of $(\langle 5d|\, r\, |4f\rangle_{\text{eff}}\, \chi)$ with refractive index. The experimental values are plotted as '*' with a 10% error bar to guide eyes. The solid curve is calculated with virtual-cavity model using best least-square-fitting value $\langle 5d|\, r\, |4f\rangle_{\text{eff}} = 0.0281$, and the dashed curve is for real-cavity model with $\langle 5d|\, r\, |4f\rangle'_{\text{eff}} = 0.0341$.